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RECOVERY OF HIGH MOLECULAR HYDROCARBONS FROM SYNTHESIS GAS AND PHYSICO-CHEMICAL CHARACTERISTICS OF THE CATALYST

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Annotation

In the article, the reaction of obtaining high molecular hydrocarbons from synthesis gas and the physicochemical characteristics of the Co-Fe-Ni-SiO2/YuKTs catalyst used in this process are studied. The increase in selectivity in methane formation is, on the one hand, the result of the acceleration of the hydrogenation reaction of CO in the centers of methane formation due to the increase in the synthesis temperature and the diffusion of CO and N2 at different speeds through the pores of zeolite. A large amount of products of secondary changes (cracking, isomerization) - isoparaffins and olefins - was found in all fractions of hydrocarbons synthesized in the presence of hybrid catalysts. The largest amount of isoparaffins was recorded for the composite catalyst - the iso/n parameter is equal to 0.6, which indicates its increased activity compared to the catalysts absorbed in the hydroremediation reactions. A higher concentration of olefins was found for catalysts with low cobalt content, which is due to their low hydrogenation capacity compared to unsaturated hydrocarbons. In absorbent catalysts, hydrocarbon synthesis centers and zeolitic acid sites are in close contact with each other, which should contribute to the enhancement of secondary processes.

Key words

syngas, high molecular hydrocarbons, catalyst, IR spectrum, diffractogram.

INTRODUCTION

GTL technology is one of the most promising methods of obtaining motor fuel from carbon-containing materials as an alternative to oil. Unlike petroleum products, synthetic fuels practically do not contain aromatic mono- and polycyclic compounds, organic sulfur and nitrogen compounds, and are ecologically clean, high-quality consumable fuel [1-5]. In nature, the raw material base of synthetic fuel is widely spread, and they consist of carbon-containing materials - natural, petroleum gases, coal, biomass, etc. [6-11]. GTL technology includes the following stages: obtaining synthesis gas (mixture of CO2 and H2); catalytic conversion of synthesis gas into hydrocarbons by the Fischer-Tropsch method; separation of products into gasoline (S5-S10), diesel (S11-S18), wax (S19+) fractions [12-16].

LITERATURE ANALYSIS AND METHODS

The main stage of GTL technology is the catalytic conversion of syngas into hydrocarbons by the Fischer-Tropsch method (FT-synthesis). Cobalt, nickel, ruthenium, iron, etc., from group VIII metals with variable valence, show catalytic activity in the catalytic conversion of synthesis gas into hydrocarbons. Cr, Mo, W from group VI metals, Mb, Te, Re from group VII metals, and Cu, Ag, Au from group IV metals increase the activity level of the catalyst to some extent [17-21].

Basically, 2 types of FT-synthesis are used in industry: low-temperature and high-temperature options [22-23]. Low temperature synthesis (LTFT) is carried out on cobalt or iron catalysts at temperatures below 300oC. In this, high molecular weight n-paraffins, n-olfins and components containing oxygen are formed. High temperature synthesis (NTFT) is carried out on an iron catalyst at temperatures above 300oC. The product consists mainly of a mixture of hydrocarbons with a high olefin content, which are used as basic raw materials for many chemical processes.

Compared to FT-synthesis products, it is characterized by the lack of isoparaffins, therefore, the synthesized hydrocarbons have a low octane number. Due to the low cloud point and filtration temperature of the diesel fraction, it is difficult to use these components as fuel. Therefore, in both options, it is necessary to change the composition of the raw materials obtained in the production of motor fuel, they are hydrolyzed using a combination of processes, cracking, isomerization and other processes according to the technological scheme [19-23].

In order to demonstrate the competitiveness of the GTL technology for obtaining motor fuel in the traditional way, it is desirable to intensify the process of each stage. One of the solutions to this problem is to combine the hydrocarbon synthesis and hydrotreating steps in a single reactor. For this, it is necessary to develop new efficient hybrid catalysts.

Block-module mobile technology in the GTL technological process allows simple equipment to be used in the processing of oil satellite gases and low-pressure gases of used gas fields in mine conditions. On such a relatively small scale, GTL technologies and equipment were developed by Compact GTL, Velocys, Chevron, Infratekhnologiya, Gazokhim Techno companies [15-22].

RESULTS

Catalytic properties of catalysts in the synthesis of hydrocarbons from CO and N2 were investigated in a flow isothermal reactor filled with 30 cm3 of quartz (catalyst layer 10 cm3) under the following optimal conditions: temperature range 280-300°C, 0.5 MPa and volumetric gas flow rate (GHT) 1000 h- 1. Balanced experiments were carried out for at least 150 hours, the composition of the incoming and outgoing gas was analyzed, and the obtained hydrocarbons and water of reaction were quantified.

The activity of hydrocarbon synthesis catalysts was evaluated according to the following parameters: CO conversion, selectivity and productivity for hydrocarbons. The calculation error did not exceed 2.5%. CO conversion was calculated according to the following formula:

$$\mathrm{X_{CO}}\,\frac{\mathrm{V_{vx}\circ c(CO)_{vx-}\,Vvix\circ c(CO)_{vix}}}{\mathrm{V_{vx}\circ c(CO)_{vx}}}\cdot 100\%$$

where Vkir, Vchik - gas consumption at the entrance to the reactor and at the exit from the reactor, dm3/h;

c(CO) input, c(CO) output - concentration of CO at the inlet and outlet of the reactor, unit percentage.

Methane selectivity was calculated according to the following formula:

$$S_{CH4=}\frac{V(CO)_{CH4}}{V(CO)_{np}}\cdot 100\%$$

where V(CO)CH4 is the volume of CO used to produce methane, dm3; In (CO)ma

- volume of CO converted into methane, dm3.

The yield of C5+ hydrocarbons was calculated using the following formula:

$$G_{C5+}=\frac{m_{C5+}}{V_{kam\cdot\tau}}$$

where mC5+ is the mass of C5+ hydrocarbons, kg; Roll – catalyst volume, m3; t - time, hour.

Determination of the composition of synthesis products. The composition of the gaseous synthesis products was analyzed by gas adsorption chromatography on two columns with the active phase Hysep R and NaX molecular sieves in a Kristall 5000 chromatograph (Khromatek, Russia) equipped with a thermal conductivity detector. The analysis mode is programmed by temperature with a heating rate of 8°C/min.The composition of C5+ hydrocarbons was determined by capillary gas-liquid chromium mass spectrometry using a gas chromatograph (Agilent, USA) equipped with an MSD 5975C mass selective detector.

DISCUSSION

The study of the catalytic properties of samples in the synthesis of hydrocarbons from CO and N2 was carried out at a temperature of 290°C, a pressure of 0.5 MPa, a gas volumetric velocity of 1000 h-1 and a ratio of N2/CO = 2. A high-silica zeolite obtained from Navbakhor bentonite was used as a catalyst-holding substance [24-29]. The experimental data obtained are presented.

Analysis of the dependence of the CO conversion rate on the synthesis temperature shows that the composite catalyst exhibits higher activity in FT synthesis than absorption catalysts. Despite the decrease in cobalt concentration by 3 times, the increase in FT synthesis temperature to 290°C in the presence of the composite catalyst increases the degree of CO conversion by 74.2% and allows achieving a productivity of 91.7 kg/m3cat·h for C5+ hydrocarbons. It can be compared with similar indicators for the FT synthesis catalyst Co-Fe-Ni-SiO2/SCC (Table 1).

Table 1.

Catalyst test results

Catalyst	C_{Co}, %	T, °C	X_{CO}, %	selectivity, %				GC5+, kg/m3 half·h
				CH_4	C_2-C_4	CO_2	C_{5+}	
Co-Fe-Ni-ZrO$_2$/ЮКЦ	20,8	225	76,2	16,1	10,4	1,4	72,1	115,0

Note: XSO is the CO conversion rate; Performance for hydrocarbons GC5+-C5+.

Samples of hybrid catalysts are characterized by a decrease in the selectivity of the formation of C5+ hydrocarbons to a level of 58-66% compared to the Co-Fe-Ni-SiO2/SC catalyst. This is due to the intensification of intermediate processes - the formation of methane and C2-C4 hydrocarbons, and the reaction of water gas.

The increase in the selectivity of methane formation is, on the one hand, the result of accelerating the reaction of CO hydrogenation in the centers of methane formation due to an increase in the synthesis temperature and diffusion of CO and H2 at different rates through the zeolite pores. [114, 116, 154].

As we already mentioned above, the FT synthesis catalyst Co-Fe-Ni-SiO2/SCC was developed for the synthesis of high molecular weight hydrocarbons (C19+), so their content in C5+ hydrocarbons reaches 46.7% (Table 2). The group composition of S5+ hydrocarbons is represented by paraffins of normal composition, the amount of isoparaffins and olefins does not exceed 3%. The molecular weight distribution of hydrocarbons is shown in Figure 1 below. In a diagram showing the distribution of the amount of hydrocarbons produced by the number of carbon atoms in the molecule, the main part of the obtained hydrocarbons includes up to 25 carbon atoms, and an important part - 25-35. The fractional composition of S5+ hydrocarbons obtained using hybrid catalysts is mainly represented by liquid hydrocarbons (S5-S18), their content is 83% for absorbent catalysts and 95% for composite catalysts. This mainly occurs due to the cracking of S19+ hydrocarbons in the acid center of the zeolite. Against the background of a decrease in the amount of hydrocarbons S19+ and partially S11-S18, an increase in hydrocarbons S5-S10 by 24-34% was noted in comparison with their composition, a redistribution of synthesis products of products obtained with the participation of the FT synthesis catalyst Co-Fe-Ni-SiO2/SCC .

Table 2.

Composition of the obtained hydrocarbons S5+

Catalyst	Hydrocarbon	Content, %			Total	iso/n
		C_5-C_{10}	C_{11}-C_{18}	C_{19+}		
Co-Fe-Ni-ZrO_2/ЮКЦ	n-paraffins	17,2	34,7	45,5	97,4	0,02
	isoparaffins	0,4	0,6	0,8	1,8	
	olefins	0,1	0,3	0,4	0,8	
	Total	17,7	35,6	46,7	100	

Note: iso/n is the ratio of isoparaffins:paraffins.

A large number of products of secondary transformations (cracking, isomerization) - isoparaffins and olefins - were found in all fractions of hydrocarbons synthesized in the presence of hybrid catalysts. The largest amount of isoparaffins was recorded in the composite catalyst - the iso/n parameter is 0.6, which indicates its increased activity compared to catalysts absorbed in hydroremediation reactions. Higher olefin concentrations were found for catalysts with lower cobalt content, this is due to their lower hydrogenation ability compared to unsaturated hydrocarbons.

The use of the absorption method for the preparation of hybrid catalysts produces a system that exhibits lower catalytic properties than the composite catalyst during the synthesis of hydrocarbons. This is probably due to both diffusion factors, pore blocking by precipitated cobalt, and the formation of compounds of cobalt and aluminum oxides that are difficult to recover from oxide-oxide interactions.

In absorbent catalysts, hydrocarbon synthesis centers and zeolitic acid sites are in close contact with each other, which should contribute to the enhancement of secondary processes. At the same time, the amount of liquid hydrocarbons (S5-S18) in the composition of S5+ hydrocarbons is about 83%, which is 12% less than that of the composite catalyst. For the composite catalyst prepared by mixing the components, no oxide-oxide interaction was found, the pores of the zeolite are not blocked by cobalt, which allows for efficient delivery of reactants to the active part of hydrocarbon synthesis.

Such a catalyst has high activity in the synthesis of hydrocarbons - the conversion rate of CO is 74.2%, the productivity and selectivity for C5 + hydrocarbons is 91.7 kg/m3cat ·h and 66.5%.

In the silica-based composite catalyst, the acid center is not blocked by the cobalt located on the silica in the Co-Fe-Ni-SiO2/YuKTs catalyst. There are both external and internal centers for hydrocarbons, as a result of which the composite catalyst increases the activity in hydrolysis reactions - the amount of liquid hydrocarbons reaches 95%. In this context, the preferred method for the preparation of hybrid catalysts is to mix the active components using a binder.

Structure and phase composition of catalysts

The phase composition and structure of the catalysts were studied using RFA and IR spectroscopy. The radiographic image is the same for all samples

The size of Co3O4 particles varies in the range of 10-12 nm, there are no deviations in the unit cell parameter of the Co3O4 structure at the level of 8.088 Å due to the change in the components of the catalyst.

CONCLUSION

Thus, the reaction of obtaining high molecular hydrocarbons from syngas and the physicochemical characteristics of the Co-Fe-Ni-ZrO2/YuKTs catalyst used in this process were studied. The increase in selectivity in methane formation is, on the one hand, the result of the acceleration of the hydrogenation reaction of CO in the centers of methane formation due to the increase in the synthesis temperature and the diffusion of CO and H2 at different speeds through the pores of zeolite. A large amount of products of secondary changes (cracking, isomerization) - isoparaffins and olefins - was found in all fractions of hydrocarbons synthesized with the presence of hybrid catalysts. The largest amount of isoparaffins was recorded for the composite catalyst - the iso/n parameter is equal to 0.6, which indicates that it has increased activity compared to the catalysts absorbed in the hydroremediation reactions. A higher concentration of olefins was found for catalysts with low cobalt content, which is due to their low hydrogenation capacity compared to unsaturated hydrocarbons. In absorbent catalysts, hydrocarbon synthesis centers and zeolitic acid sites are in close contact with each other, which should contribute to the enhancement of secondary processes. At the same time, the amount of liquid hydrocarbons (S5-S18) in the composition of S5+ hydrocarbons is about 83%, which is 12% less than that of the composite catalyst.

For the composite catalyst prepared by mixing the components, no oxide-oxide interaction was found, the pores of the zeolite are not blocked by cobalt, which allows for efficient delivery of reactants to the active part of hydrocarbon synthesis.

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